

**TITLE:** SEARCH FOR MAGNETISM IN hcp Epsilon-Fe

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# Search for magnetism in hcp $\epsilon$ -Fe<sup>a)</sup>

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## ABSTRACT

We report the results of our recent experimental investigation which extends the search for magnetic ordering in the high-pressure, hcp phase of iron ( $\epsilon$ -phase) to a temperature of 0.030 K. Mössbauer effect measurements were performed in the pressure range from atmospheric pressure to 21.5 GPa on a foil of natural iron (doped with <sup>57</sup>Co). Measurements were made of the properties of both the  $\alpha$ - and  $\epsilon$ -phase constituents of the sample. No measurable magnetic hyperfine field was observed in the  $\epsilon$ -phase from any of the spectra at pressures as high as 21.5 GPa and temperatures as low as 0.030 K.

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For more than twenty-five years, it has been known that iron undergoes a transition from the familiar  $\alpha$ -phase (bcc) to the high-pressure  $\epsilon$ -phase (hcp). Since the discovery of this transformation by Bancroft *et al.*(1) the effects of pressure on many properties of  $\alpha$ - and  $\epsilon$ -Fe have been studied extensively(2-4).

One of the most striking features of  $\epsilon$ -Fe is its nonmagnetic behavior. Mössbauer effect experiments(5) have shown that, at room temperature,  $\epsilon$ -Fe exhibits no hyperfine magnetic field at any pressure up to 24 GPa. Subsequent Mössbauer effect (ME) and neutron diffraction studies on related alloy systems(6,7) have been extrapolated to predict antiferromagnetic ordering in hcp-Fe at sufficiently low temperatures; however, band structure calculations by Fletcher and Addis(8) predict that  $\epsilon$ -Fe should not order.

Several attempts have already been made to detect magnetic ordering in  $\epsilon$ -Fe at reduced temperatures, all of which obtained negative results. These include the ME studies of Williamson *et al.*(9) and König *et al.*(10). Previous to this work the lowest temperature at which  $\epsilon$ -Fe has been investigated was 2.2 K (10).

We report here preliminary results of our experimental investigation using the Mössbauer effect of <sup>57</sup>Fe as a magnetic hyperfine field microprobe of the  $\epsilon$ -phase of iron. The primary

motivation for this work has been to extend the search for magnetic ordering in  $\epsilon$ -Fe to temperatures significantly lower than have been investigated previously, indeed, into the millikelvin range.

The Mössbauer effect of  $^{57}\text{Fe}$  is a particularly powerful tool for investigating the magnetic properties of  $\epsilon$ -Fe. In addition to providing direct measurements of any spontaneous hyperfine field in the sample on a microscopic scale, ME spectra can be analyzed to determine the relative abundance of  $\alpha$ - and  $\epsilon$ -phases in the sample.

The use of the Mössbauer effect also ameliorates several experimental difficulties associated with the high-pressure environment. ME sources can be made small enough to fit into the very limited space available inside the diamond-anvil pressure cell. In addition, electrical measurements, which are difficult to perform, are not necessary.

Our experiments were performed on a 0.025-mm-thick foil of 99.99% pure natural iron (obtained from Materials Research Corporation) doped with approximately 0.4 mCi of carrier-free  $^{57}\text{Co}$ , the  $^{57}\text{Fe}$  parent. The Co was electroplated onto both surfaces of the foil over an area of approximately  $0.039\text{ mm}^2$  and diffused into the host by heating at  $960^\circ\text{C}$  for 48 hours in an  $\text{Ar-H}_2$  atmosphere. The final sample disk, punched from the doped foil, had an area of about  $0.025\text{ mm}^2$  and a source activity of about 0.1 mCi. Fluorescence analysis showed that no impurities ( $> 1\%$ ) were introduced during the doping-diffusion operations.

The sample was pressurized in a Merrill-Bassett diamond-anvil cell. A 4:1 methanol:ethanol mixture was employed as the pressure-transmitting medium. Accurate determinations of the pressure in the cell were made using standard ruby fluorescence techniques. Measurements were performed to determine the wavelength of the  $H_1$  spectrographic line ( $dP/d\lambda = 2.74\text{ GPa/nm}$ ) on several ruby chips located in the high-pressure environment. For each pressurization no significant pressure variations were noted whenever more than one chip was used. This method allowed pressure measurements accurate to approximately  $\pm 0.3\text{ GPa}$ .

ME measurements were performed in zero applied magnetic field using a constant-acceleration ME

spectrometer with a room-temperature, single-line, potassium ferrocyanide absorber. The pressure cell containing the source was cooled by insertion into a

$^4\text{He}$  cryostat or by attachment to the mixing

chamber of a  $^3\text{He}$ - $^4\text{He}$  dilution refrigerator.

During the course of investigation, ME spectra from the sample were obtained for the pressure range from atmospheric to 21.5 GPa at selected temperatures from 300 to 0.030 K. During the initial stages of this study the ME spectra of pure  $\alpha$ -phase Fe were obtained as a function of pressure. The hyperfine splitting, isomer shift, and linewidth associated with each spectrum were determined by least-squares fits to the data. After the transformation to the  $\epsilon$ -phase had begun, similar parameters were obtained for the  $\epsilon$ -phase. Within the range of pressures for which the two phases coexist in the sample, the aforementioned parameters were determined for each phase. From such measurements, the fractional abundance of  $\epsilon$ -phase material in the sample was determined.

The hyperfine splitting of the ME spectra of  $\alpha$ -Fe has been observed by various authors(11-14) to decrease linearly as a function of pressure. We also observe a linear decrease in the internal magnetic field of  $\alpha$ -Fe with increasing pressure; however, we find a slope

$\partial \ln H / \partial P = (-3.15 \pm 0.09) \times 10^{-3} \text{ GPa}^{-1}$ , significantly higher than has been found previously. The origin of this difference is still under investigation.

Our results for the pressure dependence (at 300 K) of the isomer shift for  $\alpha$ -Fe are in reasonable agreement with previously published values(5,11,12,15).

Our measurements also show a linear change of the isomer shift as a function of pressure; the slope is

$(-6.5 \pm 0.5) \times 10^{-3} \text{ mm s}^{-1} \text{ GPa}^{-1}$  to be compared with published values ranging from  $-7.4 \times 10^{-3}$  to

$-8.3 \times 10^{-3} \text{ mm s}^{-1} \text{ GPa}^{-1}$ . We also observe a small linear decrease of the room-temperature linewidth of  $\alpha$ -Fe as a function of pressure. The linewidth observed was  $(0.48 \pm 0.01) \text{ mm s}^{-1}$  at atmospheric pressure and  $(0.40 \pm 0.02) \text{ mm s}^{-1}$  at 14.0 GPa. That there was no broadening with pressure confirms the contention that the sample was under nearly hydrostatic conditions.

Evidence for the presence of  $\epsilon$ -phase in the Fe sample was observed first at a pressure of 11.9 GPa.

The pressure dependence of the transformation from  $\alpha$ - to  $\epsilon$ -phase is given in Fig. 1. The transition width (10% to 90%) was observed to be approximately 5 GPa. At 21.0 GPa, the highest pressure employed at room temperature, the sample contained  $(2.1 \pm 1.4)\%$   $\alpha$ -Fe.

Fig. 1. Relative abundance of  $\epsilon$ -Fe (at 300 K) in natural iron as a function of pressure.

In the  $\epsilon$ -phase, the isomer shift and the line width of the hcp-component of each spectrum showed an appreciable pressure dependence. The room-temperature  $\epsilon$ -component linewidth also remained constant at a value of  $(0.41 \pm 0.01) \text{ mm s}^{-1}$  at all pressures above 12 GPa. The observed  $\epsilon$ -component linewidths are given in Table I.

TABLE I. Pressure- and temperature-dependence of the  $\epsilon$ -component linewidth

Pressure (GPa)	Temperature (K)	Linewidth (mm/s)
14.4	300	$0.41 \pm 0.01$
16.0	300	$0.41 \pm 0.01$
17.8	300	$0.41 \pm 0.01$
20.5	300	$0.41 \pm 0.01$
16.5	75	$0.44 \pm 0.01$
21.5	75	$0.44 \pm 0.03$
16.5	4	$0.44 \pm 0.01$
16.5	1	$0.43 \pm 0.01$
19.1	0.035	$0.43 \pm 0.01$
19.1	0.030	$0.43 \pm 0.01$

At all pressures above 12 GPa, and for temperatures below 100 K, the  $\epsilon$ -component linewidth is well characterized by the value

$(0.435 \pm 0.01) \text{ mm s}^{-1}$ ; the additional linewidth is the result of ME self-absorption by the 2.2%

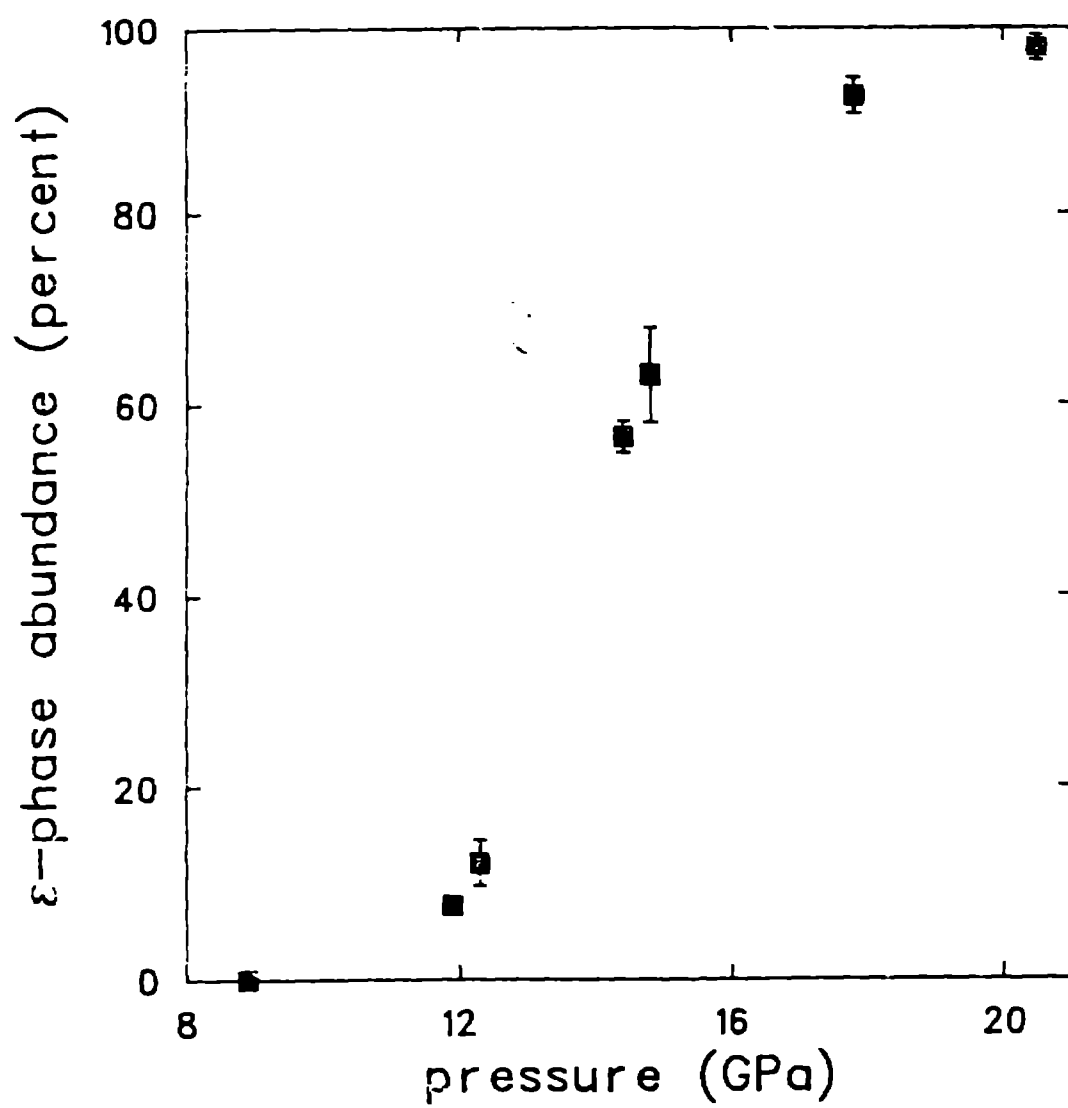
natural abundance of  $^{57}\text{Fe}$  in the source. This linewidth shows no further temperature dependence to temperatures as low as 0.030 K. We interpret this lack of measurable magnetic hyperfine splitting in the  $\epsilon$ -Fe ME spectra as evidence that the  $\epsilon$ -Fe at 19.1 GPa does not magnetically order above 0.030 K. An internal magnetic field greater than 0.05 T, arising from either ferromagnetic or antiferromagnetic ordering, could be detected by this method.

In conclusion, we have observed that  $\epsilon$ -Fe at 21.5 GPa shows no observable magnetic hyperfine field at any temperature down to 0.030 K. This result supports the band theory prediction that  $\epsilon$ -Fe does not magnetically order. ME measurements at low temperatures in applied fields up to 4 T are underway in an effort to set an upper limit on the magnetic moment of  $\epsilon$ -Fe.

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THIS DIMENSION = 4.6 INCHES